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(71) Applicant: Wm. MARSH RICE UNIVERSITY  
Houston, TX 77005-1892 (US)

(72) Inventors:

- Hirasaki, George J.  
Bellaire, Texas 77401 (US)
- Miller, Clarence A.  
Houston, 77005 (US)

(74) Representative: Wain, Christopher Paul et al

A.A. Thornton & Co.  
235 High Holborn  
London WC1V 7LE (GB)

### (54) Reducing water permeability in subterranean formation

(57) The water permeability of a water-producing zone in a subterranean formation is reduced by introducing a polymeric surfactant and an inert gas into the zone to form a water permeability reducing foam therein. The polymeric surfactant has the property of facilitating the formation of the foam and the additional property of

stabilizing the foam in the presence of flowing formation water. Examples of surfactant are ethylene oxide-propylene oxide-ethylene oxide tri-block copolymers and ethylene oxide-butylene oxide-ethylene oxide tri-block copolymers.

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**Description**

- [0001] The present invention relates to a method of reducing the water permeability of a water producing zone in a subterranean formation without substantially reducing the hydrocarbon permeability thereof.
- [0002] The production of water with hydrocarbons, i.e. oil and/or gas, from wells constitutes a major problem and expense in the production of hydrocarbons. While hydrocarbon producing wells are usually completed in hydrocarbon producing formations, when the formations contain layers of water and oil or when there are water producing zones near the hydrocarbon producing formations, the higher mobility of the water often allows it to flow into the well bores which penetrate the hydrocarbon producing formations by way of natural fractures and/or high permeability streaks.
- [0003] In the production of such wells, the ratios of water to hydrocarbons recovered often become so high that the cost of producing the water, separating it from the hydrocarbons and disposing of it represents a significant economic loss.
- [0004] In order to reduce the production of undesired water from hydrocarbon producing formations, aqueous polymer solutions containing cross-linking agents have been utilized heretofore. In the case of naturally fractured formations such aqueous polymer solutions have been pumped into the hydrocarbon producing formations so that they enter water zones within and adjacent to the formations and cross-link therein. The cross-linking of the polymer solutions causes them to form stiff gels which aid in stopping or reducing the flow of the undesired water. While the use of aqueous polymer solutions for reducing the production of undesired water has achieved varying degrees of success, the full blocking gels produced are not suitable for producing formation treatments unless the polymer solution can be placed solely in the offending water producing zone or zones therein. If a polymer solution is allowed to gel within a hydrocarbon producing zone, the cross-linked polymer gel formed will reduce or stop the flow of hydrocarbons in addition to the flow of water. The selected placement of a polymer solution in a producing formation requires expensive, time-consuming zonal isolation placement technology. In addition, even when a polymer solution is properly placed in a water producing zone, the cross-linked gels formed often do not remain stable in the zone due to thermal degradation and/or differences in the adsorption characteristics of the polymer and associated cross-linker and the like.
- [0005] More recently, chemicals referred to as relative permeability modifiers have been utilized to decrease the production of water with hydrocarbons. That is, water permeability modifying chemicals such as polyacrylamide have been introduced into hydrocarbon and water producing formations so that the chemicals attach to adsorption sites on surfaces within the porosity of the formations. The presence of the chemicals in the formations has the effect of reducing the flow of water through the formations while having a minimal affect on the flow of hydrocarbons therethrough. The use of water permeability modifying chemicals in hydrocarbon and water producing formations to decrease the production of water is considerably less expensive than other techniques such as blocking the flow of water with cross-linked polymers, and does not require expensive zonal isolation techniques. However, the use of permeability modifying chemicals has often resulted in only small reductions in water production and/or unacceptable levels of reduction in the production of hydrocarbons.
- [0006] Thus, there are needs for improved methods of treating water and hydrocarbon producing subterranean formations utilizing water permeability modifying techniques and chemicals which are more effective in reducing water production with minimal or no reduction in hydrocarbon production.
- [0007] In one aspect, the present invention provides a method of reducing the water permeability of a water producing zone in a subterranean formation penetrated by a well bore comprising introducing a polymeric surfactant and an inert gas into said water producing zone by way of said well bore to thereby form a water permeability reducing foam therein, said polymeric surfactant having the property of facilitating the formation of said foam and the additional property of stabilizing said foam in the presence of flowing formation water.
- [0008] Examples of particularly suitable polymeric surfactants useful in accordance with the present invention include, but are not limited to, ethylene oxide-propylene oxide-ethylene oxide tri-block copolymers and ethylene oxide-butylene oxide-ethylene oxide tri-block copolymers. These and other polymeric surfactants which can be utilized preferably have a molecular weight in the range of from about 5,000 to about 15,000.
- [0009] The polymeric surfactant can be introduced into the producing zone in an aqueous carrier liquid such as salt water or brine. The gas, which can be natural gas or nitrogen, is separately introduced into the producing zone in the presence of the polymeric surfactant and water therein to thereby form the water permeability reducing foam in the zone. When hydrocarbons produced in the zone contact the foam, the foam destabilizes thereby allowing the hydrocarbons to be produced, but the foam remains in the water producing portions of the zone whereby the production of water in the zone is reduced.
- [0010] The term "water" when used in reference to the water produced with hydrocarbons from subterranean formations includes fresh water, salt water and brines, preferably salt water or brines.
- [0011] In one procedure according to the present invention, for reducing the water permeability of a water and hydrocarbons producing zone in a subterranean formation penetrated by a well bore, a polymeric surfactant is introduced into the zone by way of the well bore, the surfactant having the properties of facilitating the formation of a foam, stabilizing the foam in the presence of flowing formation water and destabilizing the foam in the presence of hydrocarbons;

and then a gas is introduced into the zone by way of the well bore in the presence of the polymeric surfactant and water therein to thereby form a water permeability reducing foam in water producing portions of the zone.

[0011] As indicated above, the polymeric surfactants useful in accordance with the present invention must have the property of facilitating the formation of a foam, stabilizing the foam in the presence of flowing formation water and destabilizing the foam in the presence of hydrocarbons. It has been found that high molecular weight block polymers can have the required properties. Examples of suitable such block polymers include, but are not limited to, ethylene oxide-propylene oxide-ethylene oxide tri-block copolymers having molecular weights in the range of from about 5,000 to about 15,000 and ethylene oxide-butylene oxide-ethylene oxide tri-block copolymers having molecular weights of about 5,000 to about 15,000. A particularly suitable and presently preferred polymeric surfactant is an ethylene oxide-propylene oxide-ethylene oxide tri-block polymer having a molecular weight of about 15,000.

[0012] In accordance with the methods of this invention, the polymeric surfactant utilized is introduced into the water producing zone to be treated by way of the well bore penetrating the zone. Preferably, the polymeric surfactant is dissolved or dispersed in an aqueous carrier fluid and the carrier fluid-surfactant solution is pumped into the zone. The aqueous carrier liquid can be fresh water, an aqueous salt solution, brine or seawater. The aqueous carrier liquid is preferably salt water or brine. When salt water is used it can contain a variety of salts such as potassium chloride, sodium chloride, ammonium chloride and calcium chloride. The polymeric surfactant utilized is generally dissolved or dispersed in the aqueous carrier liquid in an amount in the range of from about 0.1% to about 5% by weight of the aqueous carrier liquid.

[0013] After the polymeric surfactant has been placed in the water producing subterranean zone, a gas for foaming water in the zone is introduced into the zone. The gas utilized is preferably natural gas or nitrogen with nitrogen being the most preferred. The gas is pumped into the zone by way of the well bore in an amount sufficient to form a foam with the aqueous solution or dispersion of the polymeric surfactant previously placed in the zone. That is, in a volumetric ratio of the gas to the aqueous solution or dispersion of the polymeric surfactant in the zone in the range of from about 1:1 to about 10:1. When the gas contacts water containing the polymeric surfactant previously introduced into the zone, a foam is formed and stabilized in the porosity of the zone. The presence of the foam substantially reduces the water flow through the zone, and because the foaming and stabilizing surfactant utilized is a high molecular weight surfactant, it is not readily leached or otherwise removed from the foam by water contact and stabilizes the foam for a long period of time. When produced hydrocarbons come into contact with the foam, the foam is destabilized and removed by the hydrocarbon flow. Thus, hydrocarbons produced in the zone readily flow through the zone, but water produced in the zone by way of fractures, permeable streaks and the like are prevented from flowing through the zone by the presence of the foam.

[0014] A preferred method of the present invention for reducing the water permeability of a water producing zone in a subterranean formation penetrated by a well bore is carried out as follows. A polymeric surfactant and an inert gas are introduced into the water producing zone by way of the well bore to thereby form a water permeability reducing foam therein, the polymeric surfactant having the property of facilitating the formation of the foam and the additional property of stabilizing the foam in the presence of flowing formation water.

[0015] Another preferred method of this invention for reducing the water permeability of a water and hydrocarbons producing zone in a subterranean formation penetrated by a well bore is as follows. An aqueous solution or dispersion of a polymeric surfactant is introduced into the zone by way of the well bore, the surfactant having the properties of facilitating the formation of a foam, stabilizing the foam in the presence of flowing formation water and destabilizing the foam in the presence of hydrocarbons. Thereafter, a gas is introduced into the zone by way of the well bore in the presence of the aqueous solution of the polymeric surfactant to thereby form a water permeability reducing foam in water producing portions of the zone.

[0016] Yet another preferred method of this invention for reducing the water permeability of a water and hydrocarbons producing zone in a subterranean formation penetrated by a well bore is as follows. An aqueous solution or dispersion of an ethylene oxide-propylene oxide-ethylene oxide block copolymer surfactant having a molecular weight in the range of from about 5,000 to about 15,000 is pumped into the zone by way of the well bore to facilitate the formation of a foam, stabilize the foam in the presence of flowing formation water and destabilize the foam in the presence of hydrocarbons, and then nitrogen gas is introduced into the zone by way of the well bore in the presence of the surfactant and water therein to thereby form a water permeability reducing foam in water producing portions of the zone.

[0017] As indicated previously, the carrier liquid is preferably salt water or brine and the polymeric surfactant is preferably present in the salt water or brine in the range of from about 0.1% to about 5% by weight of the salt water or brine. The gas utilized is preferably nitrogen gas, and the gas is preferably pumped into the zone in a volumetric ratio of the gas to the aqueous solution or dispersion of the polymeric surfactant in the zone in the range of from about 1:1 to about 10:1.

[0018] In order to further illustrate the methods of this invention, the following examples are given.

**Example 1**

[0019] Screening tests were conducted to determine the water washout times of various polymeric and other surfactants. The procedure utilized in the screening tests is as follows. Each surfactant tested was dissolved or dispersed in fresh water at a concentration of 2% surfactant by weight of water. The resulting water-surfactant mixtures were then each placed in a 1 inch diameter by 1 foot tall glass tube. Foam was generated in the glass tube by flowing air upwardly at a flow rate of 10 milliliters per minute through the water-surfactant mixture. Fresh water was then added to the top of the foam column at a flow rate of 3 milliliters per minute. The time required for the surfactant to be desorbed from the foam and for most of the foam to be washed out was measured. The various surfactants tested and the times for their washout are set forth in Table I below.

TABLE I

Surfactant Washout Tests		
Test No	Surfactant	Washout Time, min.
1	Mixture of sodium dihexylsulfosuccinate and isopropanol	2
2	Sodium dodecyl sulfate	2
3	Sodium laureth sulfate	62
4	Mixture of alkyl polyoxyethylene ether and isopropanol	3
5	Mixture of alpha olefin sulfonate and ethylene glycol monobutyl ether	3
6	Mixture of alkyl ether sulfate and ethylene glycol monobutyl ether	2
7	Mixture of alkyl amines	20
8	Ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer (EO <sub>132</sub> -PO <sub>58</sub> -EO <sub>132</sub> ) having a molecular weight of 14,600	135
9	Ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer (EO <sub>103</sub> -PO <sub>39</sub> -EO <sub>103</sub> ) having a molecular weight of 11,400	21
10	Ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer (EO <sub>76</sub> -PO <sub>30</sub> -EO <sub>76</sub> ) having a molecular weight of 8,400	100
11	Ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer (EO <sub>28</sub> -PO <sub>38</sub> -EO <sub>28</sub> ) having a molecular weight of 4,600	18
12	Ethylene oxide-butylene oxide-ethylene oxide tri-block copolymer (EO <sub>45</sub> -BO <sub>14</sub> -EO <sub>45</sub> ) having a molecular weight of 5,000	92
13	Ethylene oxide-butylene oxide-ethylene oxide tri-block copolymer (EO <sub>34</sub> -BO <sub>11</sub> -EO <sub>34</sub> ) having a molecular weight of 3,800	57

[0020] From Table I, it can be seen that the surfactants tested in Test Nos. 4, and 9 through 14 generally functioned better than the other surfactants.

**Example 2**

[0021] A number of the surfactants tested in Example 1 were tested in sand packs to determine their performance in reducing water permeability. The surfactants were dissolved or dispersed in fresh water at a concentration of 0.5% surfactant by weight of water. The resulting water-surfactant mixtures were then each used to generate a foam in a sand pack which was 1 inch in diameter by 2 feet long. That is, each water-surfactant mixture was used to form a foam in the sand pack by alternate injection of portions of the water-surfactant mixture and air. The pressure drop across the sand pack was then measured, and from the pressure drop a mobility reduction factor for liquid flow was calculated, i.e., the ratio of the pressure drop required to achieve a given volumetric flow rate with foam present to that when the sand pack was completely filled with water.

[0022] When foam with a mobility reduction factor near 100 was generated, surfactant-free 5% by weight brine was injected at a flow rate of 10 milliliters per minute and the pore volumes of water required to reduce the mobility reduction factor to a low value was measured. The various surfactants tested and the times for their washout are set forth in Table II below.

TABLE II

Sand Pack Washout Tests		
Test No.	Surfactant	Pore Volumes of Brine For Washout
1	Sodium laureth sulfate	13.5
2	Ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer ( $EO_{132}-PO_{56}-EO_{132}$ ) having a molecular weight of 14,600	27.5
3	Ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer ( $EO_{103}-PO_{36}-EO_{103}$ ) having a molecular weight of 11,400	8.0
4	Ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer ( $EO_{26}-PO_{36}-EO_{26}$ ) having a molecular weight of 4,600	5.0
5	Ethylene oxide-butylene oxide-ethylene oxide tri-block copolymer ( $EO_{45}-BO_{14}-EO_{45}$ ) having a molecular weight of 5,000	16.0

[0023] From Table II, it can be seen that the surfactants tested are effective in forming and stabilizing foams in the presence of flowing brine.

[0024] Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

#### Claims

1. A method of reducing the water permeability of a water producing zone in a subterranean formation penetrated by a well bore, which method comprises introducing a polymeric surfactant and an inert gas into said water producing zone by way of said well bore to thereby form a water permeability reducing foam therein, said polymeric surfactant having the property of facilitating the formation of said foam and the additional property of stabilizing said foam in the presence of flowing formation water.
2. A method according to claim 1, wherein said polymeric surfactant is selected from ethylene oxide-propylene oxide-ethylene oxide tri-block copolymers and ethylene oxide-butylene oxide-ethylene oxide tri-block copolymers, and is preferably an ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer having a molecular weight of from 5,000 to 15,000.
3. A method according to claim 1 or 2, wherein said polymeric surfactant is introduced into said zone as a solution or dispersion in an aqueous carrier liquid, and is preferably present in said aqueous carrier liquid in an amount of from 0.1% to 5% by weight of said carrier liquid.
4. A method according to claim 1, 2 or 3, wherein said aqueous carrier liquid is an aqueous salt solution or brine.
5. A method according to any of claims 1 to 4, wherein said polymeric surfactant and said gas are separately introduced into said zone.
6. A method according to any of claims 1 to 5, wherein said gas is natural gas or nitrogen.
7. A method according to claim 6, wherein said gas is nitrogen and it is introduced into said zone in a volumetric ratio of said gas to said aqueous solution or dispersion introduced therein of from 1:1 to 10:1.
8. A method according to any of claims 1 to 7, wherein the polymeric surfactant is introduced into said zone by way of said well bore, and the gas is introduced into said zone by way of said well bore in the presence of said polymeric surfactant and water therein to thereby form the water permeability reducing foam in water producing portions of said zone.

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9. A method according to claim 1, which comprises (a) pumping an ethylene oxide-propylene oxide-ethylene oxide tri-block copolymer surfactant into said zone in an aqueous carrier liquid by way of said well bore, and then (b) introducing nitrogen gas into said zone by way of said well bore in the presence of said surfactant and water therein to thereby form the water permeability reducing foam in water producing portions of said zone.
- 5  
10. A method according to claim 9, wherein said surfactant is present in said aqueous carrier liquid in an amount of from 0.1% to 5% by weight of said carrier liquid, and wherein said carrier liquid is preferably salt water.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 02 25 7833

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)						
X	US 4 694 906 A (HUTCHINS RICHARD D ET AL) 22 September 1987 (1987-09-22) * column 4, line 35 - line 57 * * column 6, line 3 - column 7, line 29 * * column 10, line 18 - line 65 * ---	1-18	E21B33/138 C09K7/08						
X	US 4 495 995 A (CHEN HSIU KUO ET AL) 29 January 1985 (1985-01-29) * column 2, line 22 - column 3, line 24 * ---	1-5							
A	SU 1 763 637 A (GI PROEKT I RABOTAM V NEFTYANO) 23 September 1992 (1992-09-23) Abstract ---	1							
A	SU 1 759 848 A (UK NII PRIRODNYKH GAZOV) 7 September 1992 (1992-09-07) Abstract ---	1							
A	DATABASE COMPENDEX [Online] ENGINEERING INFORMATION, INC., NEW YORK, NY, US; SEDEV R ET AL: "Foamability of PEO-PPO-PEO triblock copolymers (P85 and F108) and role of the foam films" Database accession no. E2000074966951 XP002230526 * abstract * & J DISPERSION SCI TECHNOL; JOURNAL OF DISPERSION SCIENCE AND TECHNOLOGY 1999 MARCEL DEKKER INC, NEW YORK, NY, USA, vol. 20, no. 7, 1999, pages 1759-1776, ---	2	TECHNICAL FIELDS SEARCHED (Int.Cl.) E21B C09K						
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<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>MUNICH</td> <td>10 February 2003</td> <td>Zimpfer, E</td> </tr> </table> <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone      Y : particularly relevant if combined with another document of the same category      A : technological background      O : non-patent disclosure      P : intermediate document</p> <p>T : theory or principle underlying the invention      E : earlier patent document, but published on, or after the filing date      D : document cited in the application      L : document cited for other reasons      B : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	MUNICH	10 February 2003	Zimpfer, E
Place of search	Date of completion of the search	Examiner							
MUNICH	10 February 2003	Zimpfer, E							



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## **EUROPEAN SEARCH REPORT**

Application Number  
92 25 7833

DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	<p>DATABASE COMPENDEX [Online] ENGINEERING INFORMATION, INC., NEW YORK, NY, US;</p> <p>SEDEV R ET AL: "Surface force measurement in foam films from mixtures of protein and polymeric surfactants" Database accession no. EIX99304692784 XP002230527 * abstract *</p> <p>&amp; PROCEEDINGS OF 1997 9TH INTERNATIONAL CONFERENCE ON SURFACE AND COLLOIDS SCIENCE, 9ICSCS;SOFIA, BGR JUL 6-JUL 12 1997. vol. 149, no. 1, 6 July 1997 (1997-07-06), pages 141-144, Colloids Surf Physicochem Eng Aspects;Colloids and Surfaces A: Physicochemical and Engineering Aspects Apr 15 1999 Elsevier Science Publishers B.V., Amsterdam, Netherlands -----</p>	2
TECHNICAL FIELDS SEARCHED (Int.Cl.)		
The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner
MUNICH	18 February 2003	Zimpfer, E
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10-02-2003

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 4694906	A	22-09-1987	CA EP NO	1262819 A1 0212671 A2 863473 A	14-11-1989 04-03-1987 02-03-1987
US 4495995	A	29-01-1985	CA	1197369 A1	03-12-1985
SU 1763637	A	23-09-1992	SU	1763637 A1	23-09-1992
SU 1759848	A	07-09-1992	SU	1759848 A1	07-09-1992

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